Thermodynamics and Long-Range Order of Nitrogen in γ'-Fe4N1-x

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Thermodynamics and Long-Range Order of Nitrogen in γ'-Fe_4N_{1-x}

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Models are given for the description of the chemical potential of nitrogen in γ'-Fe_4N_{1-x}. In previous work, γ'-Fe_4N_{1-x} was treated as a (sub)regular solution, thereby assuming that the N atoms are distributed randomly on the sites of their own sublattice. However, in γ'-Fe_4N_{1-x}, long-range ordering occurs of the N atoms over the sites of their own sublattice. Then, the expression for the configurational entropy should account for the occurrence of ordering. In the present article, the descriptions adopted and tested for γ'-Fe_4N_{1-x} are based on a Langmuir-type approach, the Wagner–Schottky (WS) approach, and the Gorsky–Bragg–Williams (GBW) approach. Application of the various models to data of nitrogen-absorption isotherms for the γ' iron-nitride phase shows that the subregular solution concept fails to describe the experimental data satisfactorily, whereas a very good agreement between theory and experiment is obtained for the WS and GBW approaches. It is shown that, in particular, accounting for the occupation of disorder (octahedral) sites by N atoms is necessary to obtain an accurate description of the chemical potential of nitrogen in γ'-Fe_4N_{1-x}.

I. INTRODUCTION

KNOWLEDGE of the thermodynamics of iron-nitrogen phases is of major importance for the nitriding practice of iron and low-carbon steels. Also, accurate thermodynamic data for the binary Fe-N system are a prerequisite to arrive at a useful thermodynamic description for the ternary Fe-N-C system, that plays an important role in understanding the phenomena brought about by nitriding of medium- and high-carbon steels and nitrocarburizing of iron and steels.[1]

Fe-N solid solutions can be conceived as composed of two interpenetrating sublattices: the sublattice for Fe atoms and the sublattice for N atoms. The Fe sublattice is considered to be fully occupied by Fe atoms. The N sublattice, constituted by the octahedral interstices of the Fe sublattice, is partly occupied by N atoms and partly occupied by vacancies V. In α-Fe[N] (bcc Fe sublattice) and also in γ-Fe[N] (fcc Fe sublattice), the nitrogen atoms are distributed more or less randomly over the sites of their own sublattice.[2,3] In γ'-Fe_4N_{1-x} (fcc Fe sublattice) and in ε-Fe_2N_{1-z} (hcp Fe sublattice), the nitrogen atoms show long-range order (LRO) on their own sublattice.[4–10]

Up to now, the expressions used for the Gibbs free energy of Fe-N (and Fe-N-C) phases[11–17] were based on the Hillert–Staffanson approach,[18,19] wherein the Fe-N phases are conceived as a binary (sub)regular solution of stoichiometric groups Fe_aN_c and Fe_aV_c (a and c refer to the number of (ordered) sites on each of the sublattices). Although the (sub) regular solution approach may provide a reasonable description of the thermodynamics of α-Fe[N] and γ-Fe[N], where the LRO of interstitials is absent, it is certainly inappropriate for application to γ'-Fe_4N_{1-x} and ε-Fe_2N_{1-z} phases, where pronounced LRO of the interstitial nitrogen atoms does occur.

In the calculations of the Fe-N (and also Fe-N-C) phase diagram published, the γ'-Fe_4N_{1-x} phase was usually considered to be the stoichiometric compound Fe_4N[11,12,15] or $Fe_{4.3}N$ and $Fe_{4.15}N$[13] or $Fe_{4.1}N$.[14] The homogeneity range of the γ' phase as expressed in terms of the fraction of occupied interstitial sites is of comparable magnitude as the homogeneity range of the α phase. Further, it has been well known since the pioneering work of Lehrer[20,21] that the activity of nitrogen in the γ' phase in equilibrium with an ammonia/hydrogen gas mixture changes considerably over the homogeneity range of the γ' phase. Consequently, the calculation of the Fe-N phase diagram should take into account the composition range of the γ' phase. In a recent re-evaluation of the Fe-N phase diagram, the homogeneity range of γ' was dealt with.[16,17] However, the thermodynamic model used to describe the thermodynamics of the γ' phase did not account for the LRO of the nitrogen atoms and, therefore, could not describe accurately the existing data.

In the present article, for the cubic γ' phase, the thermodynamics is modeled, taking into account the LRO. It is shown that published nitrogen-absorption isotherms, depicting the nitrogen content in a solid Fe-N phase as a function of the nitrogen activity imposed by an ammonia/hydrogen mixture, can very well be described by the Wagner–Schottky (WS) approach[22,23,24] and the Gorsky–Bragg–Williams (GBW) approach.[25,26]

II. CHEMICAL POTENTIAL OF NITROGEN IN γ'-Fe_4N_{1-x}

An equilibrium state of γ'-Fe_4N_{1-x} cannot be attained in contact with pure nitrogen gas at atmospheric pressure, because the equilibrium partial pressures of nitrogen amount to several GPa's (at normal temperatures: 500 to 1000 K). Ammonia/hydrogen gas mixtures at atmospheric pressure are

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suitable to investigate the thermodynamics of γ'-Fe_4N_{1-x} because of the wide range of high virtual nitrogen partial pressures that can be realized by variation of the ammonia content.

The chemical potential of nitrogen in a gas phase, $\mu_{N,g}$, consisting of a NH_3/H_2 mixture can be defined on the basis of the hypothetical equilibrium

$$NH_3 \rightleftarrows \frac{3}{2} H_2 + \frac{1}{2} N_2$$

where

$$\mu_{N,g} \equiv \frac{1}{2} \mu_{N_2} = \mu_{NH_3} - \frac{3}{2} \mu_{H_2}$$

If the standard states refer to unit pressure and if ideal gases or constant fugacity coefficients can be assumed, the following holds:

$$\mu_{N,g} = \frac{1}{2} G^\circ_{N_2} + \frac{1}{2} RT \ln p_{N_2} = G^\circ_{NH_3} - \frac{3}{2} G^\circ_{H_2} + RT \ln r_N \quad [1]$$

with

$$r_N = \frac{p_{NH_3}}{p_{H_2}^{3/2}}$$

where p_j refers to the partial pressure of j, the superscript o indicates the standard state of the component concerned, and r_N is the so-called nitriding potential. The virtual partial pressure of N_2 corresponding to a NH_3/H_2 mixture can be calculated from Eq. [1].

If equilibrium is attained between an imposed NH_3/H_2 mixture and γ'-Fe_4N_{1-x}, the chemical potential of nitrogen in γ'-Fe_4N_{1-x} equals that in the gas phase: $\mu_{N,\gamma'} = \mu_{N,g}$. Variation of the composition of the NH_3/H_2 gas mixture at a certain temperature and determination of the equilibrium nitrogen content in γ'-Fe_4N_{1-x} provide a so-called nitrogen-absorption isotherm for γ'-Fe_4N_{1-x}. Nitrogen-absorption isotherms allow a sensitive comparison of models describing the dependence of the chemical potential of nitrogen on the nitrogen content.

A. *Regular Solutions*

For an ideal solution of nitrogen atoms on the sublattice as constituted by the octahedral sites of fcc iron, the chemical potential of nitrogen (per mole of nitrogen atoms) is given by[27]

$$\mu_N = G^\circ_N + RT \ln \left[\frac{y_N}{1 - y_N} \right] \quad [2]$$

where G°_N is the Gibbs free energy per mole N in the reference state, y is the fraction of sites *of the interstitial sublattice* that is occupied by N atoms, R is the gas constant, and T is the absolute temperature.

Deviations from ideal mixing may be taken into account by the so-called excess Gibbs free energy of the regular solutions concept. In the zeroth approximation,[27,28] the excess Gibbs free energy consists of an additional enthalpy representing the pairwise interaction of nearest N neighbors on the sublattice constituted by the octahedral sites, while maintaining a random distribution of N atoms over these sites. The excess chemical potential of nitrogen (to be added to the right-hand side of Eq. [2]) is given by

$$\mu^E_N = (1 - 2y)\, W \quad [3]$$

with

$$W = \frac{Z}{2} [2e_{NV} - e_{NN} - e_{VV}]\, N_{Av}$$

where W is the so-called exchange energy; Z is the number of nearest neighboring sites on the interstitial sublattice. e_{NV}, e_{NN}, and e_{VV} are energies per pair of "atoms" in N-V, N-N, and V-V pairs, respectively, with V denoting empty sites on the interstitial sublattice. and N_{Av} is Avogadro's number.

In a subregular solution,[29,30] the excess chemical potential of nitrogen (to be added to the right-hand side of Eq. [2]) is given by

$$\mu^E_N = (1 - 2y)\, W_0 + (-1 + 6y - 6y^2)\, W_1 \quad [4]$$

where W_0 is identical to W in Eq. [3] and W_1 is an unknown, phenomenological (fitting) parameter. The subregular solution adopts the Gibbs expression for the configurational entropy, implying random mixing. If LRO occurs, this configurational entropy term should be modified. Nevertheless, using W_0 and W_1 as arbitrary temperature-dependent parameters may provide a satisfactory fit of experimental data. The latter approach was followed in References 16 and 17 for the γ' phase. In the present article, the configurational entropy term is modified.

B. *LRO Solutions*

In γ'-Fe_4N_{1-x}, the Fe atoms constitute an fcc sublattice and the N atoms reside at the octahedral interstices of the Fe sublattice. Ordering of N on the interstitial sublattice occurs in such a way that the N atoms prefer to occupy the positions of type (1/2, 1/2, 1/2) with respect to the fcc Fe sublattice, constituting one-quarter of all octahedral interstices;[4,5,7] *i.e.*, the interstitial sublattice with composition V_3N is isomorphous with the substitutional ordered phase Cu_3Au ($L1_2$).

Three different descriptions for the configurational entropy for the γ'-Fe_4N_{1-x} phase are considered: a Langmuir-type description[23,24] and the WS[22,23,24] and GBW[25,26] approximations. In the Langmuir-type description, it is assumed that one-quarter of all interstitial sites is available for occupation by N atoms, implying that the maximum N content corresponds with the stoichiometry Fe_4N. The other two descriptions, in principle, allow the occurrence of overstoichiometry (with reference to Fe_4N). Only in the GBW approach are the sites for occupation by N and V atoms defined explicitly with reference to the crystallography of the interstitial sublattice.

1. *Langmuir-type approach*

A Langmuir-type description for Fe_4N_{1-x} presupposes that one-quarter of all the octahedral sites is available for N atoms. The remainder of the octahedral sites remains empty (is occupied by atoms V). Taking the enthalpies of mixing Fe, N, and V equal to nil, and taking the configurational entropy term as for a random distribution of N and V over the quarter of the octahedral sites available for oc-

cupation by N, the following is obtained for the chemical potential of nitrogen in γ'-nitride, $\mu^{L}_{N,\gamma'}$ (the superscript L indicates Langmuir-type approach):

$$\mu^{L}_{N,\gamma'} = G^{\circ L}_{N,\gamma'} + RT \ln \left[\frac{4y_{N,\gamma'}}{1 - 4y_{N,\gamma'}} \right] \quad [5]$$

For equilibrium with an ammonia/hydrogen mixture, equating Eqs. [1] and [5] gives

$$\frac{4y_{N,\gamma'}}{1 - 4y_{N,\gamma'}} = \frac{r_N}{r^{\circ L}_{N,\gamma'}} \quad [6]$$

with $r^{\circ L}_{N,\gamma'}$ defined as $RT \ln r^{\circ L}_{N,\gamma'} = G^{\circ L}_{N,\gamma'} - G^{\circ}_{NH_3} + 3G^{\circ}_{H_2}/2$. It follows from Eq. [6] that $r^{\circ L}_{N,\gamma'}$ can be interpreted as the nitriding potential in equilibrium with γ'-Fe_4N_{1-x} having the hypothetical composition $Fe_4N_{1/2}$ ($y = 1/8$). According to Eq. [6], nitrogen-absorption isotherms conforming to the Langmuir-type behavior can be written as

$$4\Delta y_{N,\gamma'} = -4y_{N,\gamma'} \frac{r^{\circ L}_{N,\gamma'}}{r_N} \approx -\frac{r^{\circ L}_{N,\gamma'}}{r_N} \quad [7]$$

where $4\Delta y_{N,\gamma'} = 4y_{N,\gamma'} - 1$ describes the deviation of the composition from the stoichiometry Fe_4N ($Fe_4N_{1+4\Delta y_{N,\gamma'}}$); $4y_{N,\gamma'} \approx 1$. The dependence of the nitrogen content in γ'-Fe_4N_{1-x} on the nitriding potential r_N could be described reasonably well with a Langmuir-type behavior for compositions not too close to Fe_4N.[23,24,31,32] Using the data from References 31 and 32 for temperatures ranging from 673 to 873 K, the following is obtained (also discussed in the Appendix):

$$\ln r^{\circ L}_{N,\gamma'} = -9.47 - \frac{1.21 \cdot 10^3}{T} \quad [8]$$

where $r^{\circ L}_{N,\gamma'}$ is given in $Pa^{-1/2}$ and T is given in kelvin.

2. *WS approach*

The WS description for Fe_4N_{1-x}[22] presupposes that 1/4 of the octahedral sites is occupied preferably by N atoms, denoted as i sites, and that the remaining 3/4 of the octahedral sites is occupied preferably by V atoms, denoted as v sites. The crystallographic positions of the i and v sites with respect to each other are not specified. Taking the enthalpies of mixing Fe, N, and V equal to nil, and taking the configurational entropy term as for random distributions of N and V over each type of site, the following is obtained for the chemical potential of nitrogen in γ'-nitride, $\mu^{WS}_{N,\gamma'}$:

$$\mu^{WS}_{N,\gamma'} = G^{\circ WS}_{N,\gamma'} + RT \ln \left\{ \sqrt{1 + \left(\frac{\Delta y_{N,\gamma'}}{2K^{WS}_{\gamma'}} \right)^2} + \frac{\Delta y_{N,\gamma'}}{2K^{WS}_{\gamma'}} \right\} \quad [9]$$

where $4\Delta y_{N,\gamma'} = 4y_{N,\gamma'} - 1 = y_i + 3y_v - 1$ describes the deviation of the composition from the stoichiometry $Fe_4N(Fe_4N_{1+4\Delta y_{N,\gamma'}})$, with y_i and y_v as the fractions of sites i and v occupied by N atoms, respectively. The temperature-dependent constant $K \equiv 3y_v/4 = 1(1 - y_i)/4$ (the superscript WS and subscript γ' are omitted) has the following basis. For the exchange reaction of N atoms at i sites with N atoms at v sites, the equilibrium constant K' reads

$$K' = \left[\frac{3}{4} y_v \frac{1}{4}(1 - y_i) \right] \Big/ \left[\frac{1}{4} y_i \frac{3}{4}(1 - y_v) \right].$$

If it is assumed that a strong tendency for ordering occurs, so $y_i \approx (1 - y_v) \approx 1$. Hence, $K' \approx y_v (1 - y_i)$. For the composition corresponding to the stoichiometry Fe_4N, it holds that $y = 3y_v/4 + y_i/4 = 1/4 \Leftrightarrow 3y_v/4 = (1 - y_i)/4 \equiv K$. Hence, for relatively small deviations from the stoichiometry Fe_4N,

$$K' \approx \frac{16}{3} K^2 = y_v (1 - y_i) \quad [10]$$

Equilibrium between nitrogen on i and v sites for $y_i \neq y_v$ in the WS approach implies different reference states for N atoms at i and v sites. The associated difference of the Gibbs free energy for nitrogen atoms at i and v sites can be conceived as the driving force for ordering.

For equilibrium with an ammonia/hydrogen mixture, equating Eqs. [1] and [9] yields

$$\frac{r_N}{r^{\circ WS}_{N,\gamma'}} = \left\{ \sqrt{1 + \left(\frac{\Delta y_{N,\gamma'}}{2K^{WS}_{\gamma'}} \right)^2} + \frac{\Delta y_{N,\gamma'}}{2K^{WS}_{\gamma'}} \right\} \quad [11]$$

with $r^{\circ WS}_{N,\gamma'}$ defined as $RT \ln r^{\circ WS}_{N,\gamma'} = \mu^{\circ WS}_{N,\gamma'} - G^{\circ}_{NH_3} + 3G^{\circ}_{H_2}/2$. It follows from Eq. [11] that $r^{\circ WS}_{N,\gamma'}$ can be interpreted as the nitriding potential in equilibrium with γ'-Fe_4N_{1-x} having the hypothetical composition Fe_4N_1. The nitrogen-absorption isotherm of γ'-nitride, as given implicitly by Eq. [11], can be rewritten as (discussed in Reference 24)

$$\Delta y_{N,\gamma'} = K^{WS}_{\gamma'} \left[\frac{r_N}{r^{\circ WS}_{N,\gamma'}} - \frac{r^{\circ WS}_{N,\gamma'}}{r_N} \right] \quad [12]$$

For compositions not too close to Fe_4N, but still allowing the approximation $4y_{N,\gamma'} \approx 1$, it holds that $r^{\circ WS}_{N,\gamma'} >> r_N$ and, thus, $r^{\circ L}_{N,\gamma'} = 4K^{WS}_{\gamma'} r^{\circ WS}_{N,\gamma'}$ (*cf.* Eqs. [7] and [12]). From an evaluation of the data provided in References 23, 31, and 32 for temperatures ranging from 673 to 873 K, the following values were found for $r^{\circ WS}_{N,\gamma'}$ and $K^{WS}_{\gamma'}$ (the evaluation procedure is discussed in the Appendix):

$$\ln r^{\circ WS}_{N,\gamma'} = -12.5 + \frac{6.35 \cdot 10^3}{T} \quad [13a]$$

$$\ln 4K^{WS}_{\gamma'} = 2.98 - \frac{7.56 \cdot 10^3}{T} \quad [13b]$$

where $r^{\circ WS}_{N,\gamma'}$ is given in $Pa^{-1/2}$ and T is given in kelvin.

3. *GBW approach*

The zeroth approximation for long-range ordering or the GBW approximation[25,26] applied to ordering of the N atoms on the sublattice of the octahedral interstices in fcc Fe involves incorporation of pairwise interaction of nearest neighboring atoms on the sublattice for N atoms (*i.e.*, N-N, N-V, and V-V pairwise interactions are taken into account). Adopting the same distinction between i and v sites as given in Section 2 for the WS approach but now specifying their crystallographic positions, i sites are sites of type (1/2, 1/2, 1/2) and v sites are sites of type (1/2, 0, 0), the following can be derived for the chemical potential of nitrogen on the i sites in γ'-nitride, ${}^{i}\mu^{GBW}_{N,\gamma'}$:

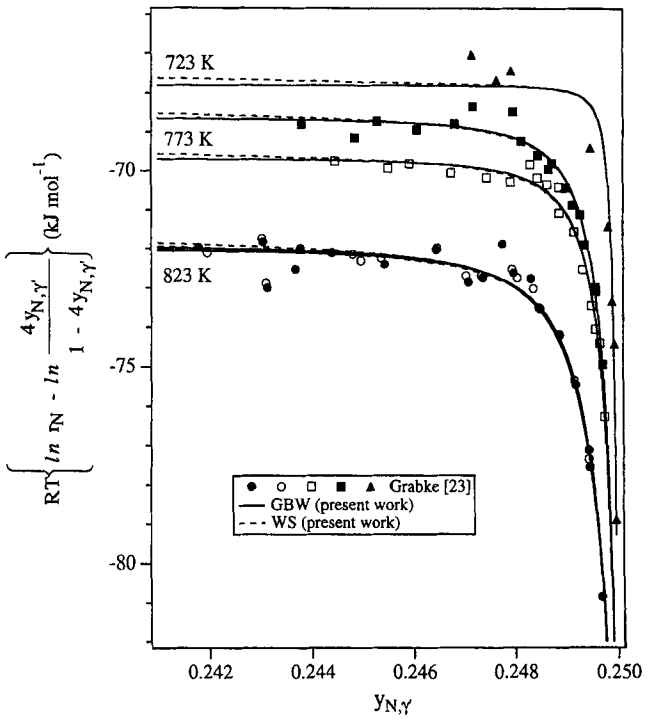

Fig. 1—Experimental data of the nitriding potential for γ'-Fe_4N_{1-x}, $r_{N,\gamma'}$, as a function of the fraction occupied interstitial sites, $y_{N,\gamma'}$, at 823, 773, and 723 K (data from Ref. 23). RT ln $r_{N,\gamma'}$ is given relative to the configurational entropy (times T) according to the Langmuir-type approach for γ'-Fe_4N_{1-x} (refer to text and Eq. [18]). Dashed and solid lines represent the results obtained by fitting the WS approach and the GBW approach, respectively, to the data sets (at 823 and 773 K, two data sets are available: filled and open markers).

$$ {}^{i}\mu^{GBW}_{N,\gamma'} = G^{\circ,GBW}_{N,\gamma'} + RT \ln \frac{{}^{i}y_{N,\gamma'}}{1 - {}^{i}y_{N,\gamma'}} + W_{N,\gamma'}(1 - 2{}^{v}y_{N,\gamma'}) \quad [14a] $$

and for the chemical potential of nitrogen on the v sites in γ'-nitride, ${}^{v}\mu^{GBW}_{N,\gamma'}$:

$$ {}^{v}\mu^{GBW}_{N,\gamma'} = G^{\circ,GBW}_{N,\gamma'} + RT \ln \frac{{}^{v}y_{N,\gamma'}}{1 - {}^{v}y_{N,\gamma'}} + W_{N,\gamma'}(1 - 2{}^{i}y_{N,\gamma'}) \quad [14b] $$

where $W_{N,\gamma'}$ is the exchange energy for nearest neighbors on the interstitial sublattice in γ'-nitride (*cf.* Eq. [3]). Equilibrium implies that ${}^{i}\mu^{GBW}_{N,\gamma'} = {}^{v}\mu^{GBW}_{N,\gamma'}$, which results in an equilibrium condition nonlinear in ${}^{i}y_{N,\gamma'}$, and ${}^{v}y_{N,\gamma'}$. The fraction of the interstitial sublattice that is occupied by nitrogen atoms, $y_{N,\gamma'}$, is

$$ y_{N,\gamma'} = \frac{1}{4}{}^{i}y_{N,\gamma'} + \frac{3}{4}{}^{v}y_{N,\gamma'} \quad [15] $$

For equilibrium with an ammonia/hydrogen mixture, equating Eqs. [1] and [14a] yields

$$ \ln \frac{r_N}{r^{\circ,GBW}_{N,\gamma'}} = \ln \left[\frac{{}^{i}y_{N,\gamma'}}{1 - {}^{i}y_{N,\gamma'}} \right] + (1 - 2{}^{v}y_{N,\gamma'}) \frac{W_{N,\gamma'}}{RT} \quad [16] $$

with $r^{\circ,GBW}_{N,\gamma'}$ defined as RT ln $r^{\circ,GBW}_{N,\gamma'} = G^{\circ,GBW}_{N,\gamma'} - G^{\circ}_{NH_3} + 3G^{\circ}_{H_2}/2$. It follows from Eq. [16] that $r^{\circ,GBW}_{N,\gamma'}$ can be interpreted as the nitriding potential in equilibrium with γ'-Fe_4N_{1-x} having the hypothetical composition Fe_4N_2 and ${}^{i}y_{N,\gamma'} = {}^{v}y_{N,\gamma'} = 1/2$ (*i.e.*, a random distribution of N atoms over all available sites). Comparing Eqs. [6] and [16], it follows that $r^{\circ,L}_{N,\gamma'} = r^{\circ,GBW}_{N,\gamma'} \exp\left[\frac{W_{N,\gamma'}}{RT}\right]$ for ${}^{v}y_{N,\gamma'} \to 0$.

In combination with the equilibrium condition ${}^{i}\mu^{GBW}_{N,\gamma'} = {}^{v}\mu^{GBW}_{N,\gamma'}$, (Eqs. [14a] and [14b]), experimental nitrogen-absorption isotherms can be characterized by values for the constants $r^{\circ,GBW}_{N,\gamma'}$ and $W_{N,\gamma'}$. To arrive at values for the occupancies ${}^{i}y_{N,\gamma'}$ and ${}^{v}y_{N,\gamma'}$, the following procedure was pursued. For chosen values of the exchange energy $W_{N,\gamma'}/RT$ and the fraction ${}^{i}y_{N,\gamma'}$, the value of ${}^{v}y_{N,\gamma'}$ was determined from the equilibrium condition using the Newton(–Raphson) method[33] and, subsequently, a value for $y_{N,\gamma'}$ was obtained from Eq. [15]. Then, by keeping $W_{N,\gamma'}/RT$ constant and varying the value for ${}^{i}y_{N,\gamma'}$, the range of corresponding values for ${}^{v}y_{N,\gamma'}$ (and $y_{N,\gamma'}$) was obtained. Substitution of these values into Eq. [16] provided the shape of a plot of ln $(r_N/r^{\circ,GBW}_{N,\gamma'})$ *vs* $y_{N,\gamma'}$, which is fully governed by the value for $W_{N,\gamma'}/RT$. The absolute level (with respect to the ordinate) of the curve is determined by the value for $r^{\circ,GBW}_{N,\gamma'}$. Using the same experimental data as for the WS approach, the following values for $W_{N,\gamma'}/RT$ and $r^{\circ,GBW}_{N,\gamma'}$ were obtained (the evaluation procedure is discussed in the Appendix):

$$ \ln r^{\circ,GBW}_{N,\gamma'} = -26.4 + \frac{24.8 \cdot 10^3}{T} \quad [17a] $$

$$ \frac{W_{N,\gamma'}}{RT} = 16.9 - \frac{29.0 \cdot 10^3}{T} \quad [17b] $$

where $r^{\circ,WS}_{N,\gamma'}$ is given in $Pa^{-1/2}$ and T is given in kelvin. Using Eqs. [17] and ${}^{i}\mu^{GBW}_{N,\gamma'} = {}^{v}\mu^{GBW}_{N,\gamma'}$ (*cf.* Eq. [14]), nitrogen-absorption isotherms as prescribed by the GBW approach are obtained with Eq. [16].

III. COMPARISON OF MODEL PREDICTIONS WITH EXPERIMENTAL DATA

A. *LRO Solutions*

It has been shown for compositions not too close to the stoichiometric composition that the nitrogen-absorption isotherm of γ'-nitride can be described reasonably well by the Langmuir-type approach (Eqs. [6] and [8]). Therefore, a sensitive comparison of the various models (L, WS, and GBW) is obtained if the nitrogen-absorption isotherms as described by the the WS approach and by the GBW approach are considered as a function of $y_{N,\gamma'}$ relative to the nitrogen-absorption isotherms as described by the Langmuir-type approach; *i.e.*, $f(y_{N,\gamma'})$ is studied with (*cf.* Eq. [6])

$$ f(y_{N,\gamma'}) = \ln r_N - \ln \left[\frac{4y_{N,\gamma'}}{1 - 4y_{N,\gamma'}} \right] \quad [18] $$

The experimental data of Reference 23 are given in Figure 1. The data cover the entire homogeneity range of γ'-Fe_4N_{1-x} for the temperatures 673, 723, and 773 K. As follows from Eqs. [6] and [18], Langmuir-type behavior for γ'-Fe_4N_{1-x} implies that all data in Figure 1 are on a horizontal line (at the ordinate value ln $r^{\circ,L}_{N,\gamma'}$). Approaching the stoichiometry Fe_4N, the experimental data clearly deviate from such behavior. The lines given in Figure 1 represent the results obtained by fitting the WS and the GBW ap-

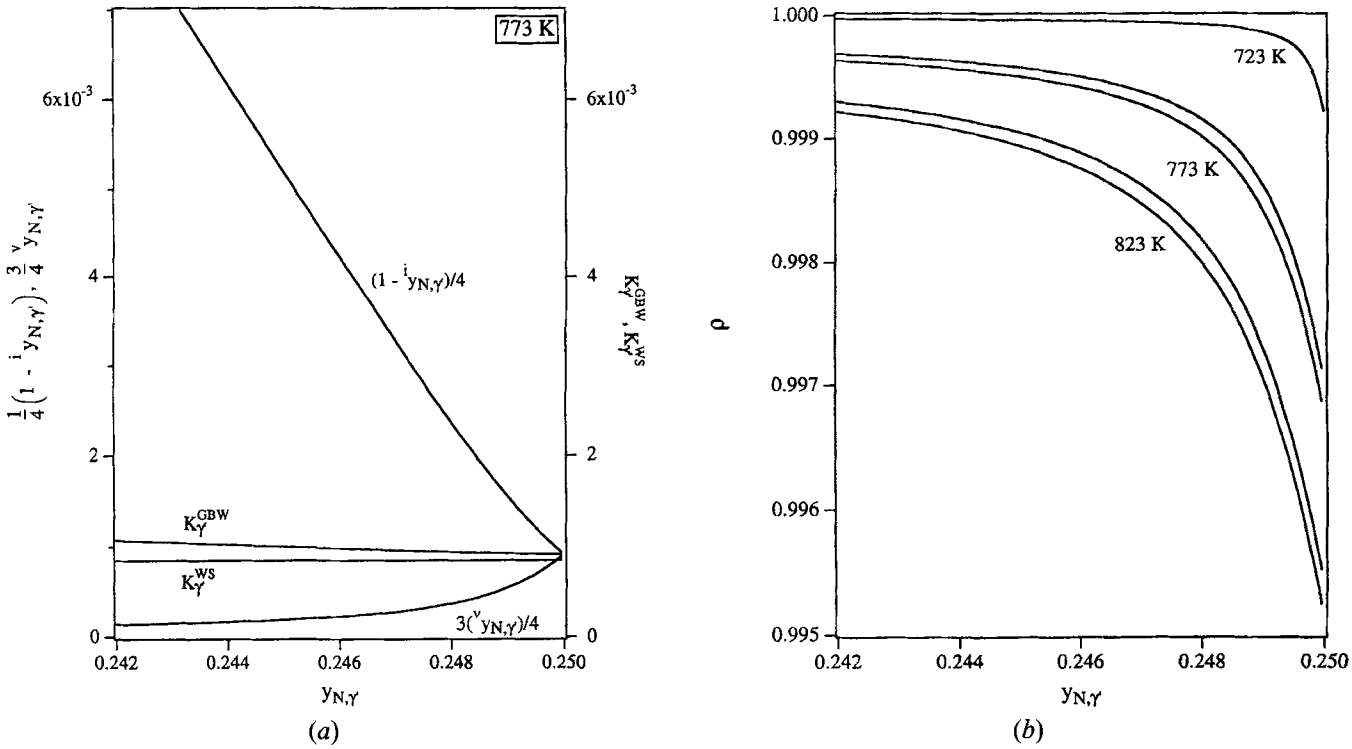

Fig. 2—(*a*) The fraction of empty (ordered) *i* sites, $1(1 - {}^{i}y_{N,\gamma'})/4$, and the fraction of occupied *v* sites, $3{}^{v}y_{N,\gamma'}/4$, for γ'-Fe_4N_{1-x} as a function of the total occupied fraction of the nitrogen sublattice, $y_{N,\gamma'}$, as calculated from the value for $W_{N,\gamma'}/RT$ obtained from fitting the GBW approach to the 773 K data of Ref. 23. The square root of the product of $1(1 - {}^{i}y_{N,\gamma'})/4$ and $3{}^{v}y_{N,\gamma'}/4$, denoted as $K_{\gamma'}^{GBW}$, can be compared to $K_{\gamma'}^{WS}$, as obtained from fitting the WS approach to the 773 K data of Ref. 23. (*b*) The degree of order ρ (for definition see text) for γ'-Fe_4N_{1-x} at temperatures of 823, 773, and 723 K as a function of the fraction occupied interstitial sites, $y_{N,\gamma'}$, as obtained from fitting the GBW approach in combination with equilibrium between *i* and *v* sites to the experimental data shown in Fig. 1. The double lines given for 823 and 773 K reflect the slight difference between the results of the two data sets at these temperatures.

proaches to the experimental data* (using the downhill simplex method[34]).

*For the GBW approach, the fitting in Fig. 1 is identical to that performed for the determination of Eq. [17]. However, a corresponding remark does not hold for the WS approach (refer to the procedure used to determine Eq. [13] in the Appendix). In order to enable fair comparison between the WS and GBW approaches, the fitting of the WS approach for the same set of data was repeated using the same procedure as for the GBW approach.

It is found that both the WS and GBW approaches provide an excellent description of the experimental data, also close to the stoichiometric composition Fe_4N where strong curvature in $f(y_{N,\gamma'})$ occurs (*cf.* Figure 1). It can be concluded that accounting for the occupation of *v* sites by N atoms is important for a good description of (the configurational entropy terms in) the thermodynamics. Despite the theoretical superiority of the GBW approach as compared to the WS approach, for the present case, the GBW approach does not give a better quantitative description of the experimental data than the WS approach. Evidently, $K_{\gamma'}^{WS}$ is practically constant and the use of Eq. [10] is justified for the present case. The validity of Eq. [10] can be further substantiated by considering the fraction of empty (ordered) nitrogen sites, $(1 - {}^{i}y_{N,\gamma'})$, and the fraction of occupied vacant sites, ${}^{v}y_{N,\gamma'}$, as obtained with the GBW approach. For the data from Reference 24 at 773 K, it holds that $W_{N,\gamma'}/RT = -20.6$ (Eq. [17b]); the corresponding fractions $1(1 - {}^{i}y_{N,\gamma'})/4$ and $3{}^{v}y_{N,\gamma'}/4$ are given in Figure 2(a). Using Eq. [10], a value for K is obtained and is denoted as $K_{\gamma'}^{GBW}$ in Figure 2(a). The line indicated by $K_{\gamma'}^{WS}$ describes the experimental data according to direct fitting of the WS approach (see preceding asterisked note). Indeed, $K_{\gamma'}^{GBW}$ varies only slightly over the homogeneity range investigated and is almost identical to $K_{\gamma'}^{WS}$. Further, the degree of order ρ, defined as

$$\rho = \left[\frac{{}^{i}y_{N,\gamma'} - {}^{v}y_{N,\gamma'}}{{}^{i}y_{N,\gamma'} + 3{}^{v}y_{N,\gamma'}}\right]$$

is given in Figure 2(b) for the experimental values for $W_{N,\gamma'}/RT$. Since the values for ρ are close to unity, the interstitial ordering in γ'-Fe_4N_{1-x} for the temperatures considered is almost perfect; obviously, ρ decreases with increasing temperature. It can be concluded that the validity of Eq. [10] for the present case is due to (1) the narrow homogeneity range of the γ'-Fe_4N_{1-x} phase close to the stoichiometry Fe_4N and (2) a degree of order that is close to unity.

B. *Long-Range Order Solution vs Subregular Solution*

Recently, a thermodynamic description of the γ'-Fe_4N_{1-x} phase was presented, where γ'-Fe_4N_{1-x} is conceived as a subregular solution (SRS) of groups Fe_4N and Fe_4V.[16,17] This implies that (1) one-quarter of all octahedral sites is available for a random distribution of N atoms, *i.e.*, Langmuir-type approach for γ'-Fe_4N_{1-x}, and (2) an arbitrary excess Gibbs free energy expression is introduced according

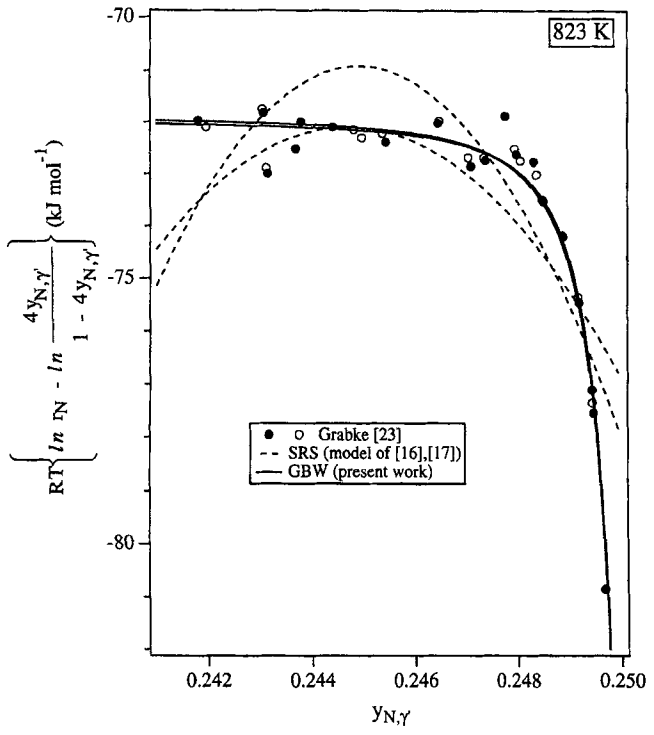

Fig. 3—Experimental data of the nitriding potential for γ'-Fe_4N_{1-x}, $r_{N,\gamma'}$, as a function of the fraction occupied interstitial sites, $y_{N,\gamma'}$, at 823 K (data from Reference 23); presentation as in Figure 1. The solid lines represent the results obtained by fitting the GBW approach to the two data sets at 823 K (filled and open dots; *cf.* Figure 1). The dashed lines represent the optimized fits for the SRS model to the two sets of data as used for the γ'-Fe_4N_{1-x} phase in Refs. 16 and 17.

to the subregular solution (*cf.* Eq. [4]). In Figure 3, least-squares fits of such a model, denoted as SRS, to the two sets of data at 823 K of Reference 23 are given (dashed lines), together with the results obtained on fitting the GBW approach to these data sets (solid lines, *cf.* Figure 1). It is obvious that the SRS approach applied to the γ'-Fe_4N_{1-x} phase in References 16 and 17 is not capable of providing an accurate description of the experimental data, despite the fact that the SRS model, as applied in Figure 3, employs three fitting parameters instead of two as in the GBW (or the WS) approach. This result demonstrates that a possible occupation of v sites by N atoms should be considered in the thermodynamic description of the γ'-Fe_4N_{1-x} phase.

IV. CONCLUSIONS

1. In order to obtain an accurate description of the chemical potential of nitrogen in γ'-Fe_4N_{1-x}, the occupation of disorder (octahedral) sites by N atoms needs to be considered. Existing nitrogen-absorption isotherms for the γ'-Fe_4N_{1-x} phase can be very well described on the basis of the GBW approximation. Due to the narrow homogeneity range of γ' nitride close to stoichiometric Fe_4N and the high degree of order among the nitrogen atoms on their own sublattice, the theoretically less sound WS approach gives a mathematically equally good description of the nitrogen-absorption isotherms for γ' nitride.
2. Conceiving the γ'-Fe_4N_{1-x} phase as a subregular solution of groups of compositions Fe_4N and Fe_4V does not lead to a description of the absorption isotherms for γ'-Fe_4N_{1-x} that is as accurate as the GBW and WS approaches, despite the use of more fitting parameters.

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APPENDIX
Evaluation of nitrogen-absorption isotherms for γ'-Fe_4N_{1-x}

Evaluation of experimentally determined nitrogen-absorption isotherms for γ'-nitride in terms of the WS approach from a linear regression of $\Delta y_{N,\gamma'}/r_N$ *vs* $1/(r_N)^2$ yields values for $r^{\circ,WS}_{N,\gamma'}$ and $K^{WS}_{\gamma'}$ (*cf.* Eq. [12]). For the data in Reference 23, the following is obtained:

$$\ln r^{\circ,WS}_{N,\gamma'} = -9.71 + \frac{4.41 \cdot 10^3}{T} \qquad [A1a]$$

$$\ln 4K^{WS}_{\gamma'} = 2.98 - \frac{7.56 \cdot 10^3}{T} \qquad [A1b]$$

where $r^{\circ}_{N,\gamma'}$ is given in $Pa^{-1/2}$ and T is given in kelvin. Comparing the set of data of References 31 and 32, which were fitted using the Langmuir-type approach, with the set of data of Reference 23, which were fitted using the WS approach, the values for the nitriding potential of the absorption isotherms for each temperature appear to be systematically shifted. The incompatibility between these data sets is illustrated by the fact that $r^{\circ,L}_{N,\gamma'}$ (from References 31 and 32) $\neq 4K^{WS}_{\gamma'} \cdot r^{\circ,WS}_{N,\gamma'}$ (from Reference 23); refer to the text following Eq. [12]. The discrepancy can most probably be attributed to experimental difficulties in obtaining accurate nitrogen-absorption isotherms for γ'-Fe_4N_{1-x} in ammonia/hydrogen gas mixtures (highly porous foils should be used); a discussion and evaluation of the experimental procedures employed in References 23, 31, and 32 was given in Reference 35, where it was concluded that, quantitatively, the data given in References 31 and 32 are more accurate than those given in Reference 23. This conclusion is supported by the observation that extrapolation according to Langmuir-type behavior of the results from within the region where Langmuir-type behavior holds to the composition Fe_4N does not yield $\Delta y_{N,\gamma'} = 0$ for the data of Reference 23, whereas it does for the data of References 31 and 32. However, a major disadvantage of the latter, preferred data set is the lack of data close to the composition of Fe_4N, *i.e.*, in the regime where Langmuir-type behavior does not apply. Therefore, the data of Reference 23 were made compatible with the data of References 31 and 32 by taking $r^{\circ,WS}_{N,\gamma'} = r^{\circ,L}_{N,\gamma'}/4K^{WS}_{\gamma'}$ (*cf.* text following Eq. [12]) with $r^{\circ,L}_{N,\gamma'}$ derived from the data set of References 31 and 32 (*i.e.*, Eq. [8]) and $K^{WS}_{\gamma'}$, quantifying the deviation from Langmuir-type behavior, derived from the data of Reference 23 (*i.e.* Eq. [A1b]); this simple procedure for determination of $r^{\circ,WS}_{N,\gamma'}$ and $K^{WS}_{\gamma'}$ yields the same results as a systematic cor-

rection of all data points of Reference 23 individually, followed by determination of $r^{\circ,WS}_{N,\gamma'}$ and $K^{WS}_{\gamma'}$ from plots of $\Delta y_{N,\gamma'}/r_N$ *vs* $1/(r_N)^2$. Thus, the following is obtained:

$$\ln r^{\circ,WS}_{N,\gamma'} = -12.5 + \frac{6.35 \cdot 10^3}{T} \qquad [A2]$$

with T in kelvin.

Evaluation of the nitrogen-absorption isotherms for γ' nitride in terms of the GBW approach was performed in a way analogous to the preceding procedure for the WS approach. Fitting of Eq. [16] (in combination with ${}^i\mu^{GBW}_{N,\gamma'} = {}^v\mu^{GBW}_{N,\gamma'}$ (Eqs. [14a] and [14b])) to the data of Reference 23 provided the (initial) values for $r^{\circ,GBW}_{N,\gamma'}$ and $W_{N,\gamma'}/RT$. Since results for the GBW approach can only be obtained numerically (using the Newton–Raphson procedure to solve the equilibrium condition ${}^i\mu^{GBW}_{N,\gamma'} = {}^v\mu^{GBW}_{N,\gamma'}$), determination of the values for the parameters $r^{\circ,GBW}_{N,\gamma'}$ and $W_{N,\gamma'}/RT$ by a least-squares fit to the data can only be obtained using a suitable iterative procedure for minimization of (squared) differences. Such a procedure, employed here, is the downhill simplex method attributed to Nelder and Mead.[34] Next, the data of Reference 23 were made compatible with the data of References 31 and 32 (see preceding discussion) by taking $r^{\circ,GBW}_{N,\gamma'} = r^{\circ,L}_{N,\gamma'} \exp(-W_{N,\gamma'}/RT)$ (refer to the text following Eq. [16]) with $r^{\circ,L}_{N,\gamma'}$ derived from the data of References 31 and 32 (*i.e.*, Eq. [8]) and $W_{N,\gamma'}/RT$, quantifying the deviation from Langmuir-type behavior, derived from fitting the data of Reference 23. The results are given by Eqs. [17a] and [17b].

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